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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Protection against Carburisation

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to protection of furnaces or furnace tubes against carburisation.

In the well known process of catalytic tubular steam reforming of hydrocarbons a reaction mixture of hydrocarbon, e.g. vaporised naphtha, and steam is passed through tubes containing a catalyst, the reaction being carried out at elevated temperatures, e.g. 600—1000° C, and often at superatmospheric pressure, e.g. up to 50 atmospheres. In order to withstand such high temperatures under conditions of stress the tubular reactors are made of steel containing a large proportion of chromium (generally more than 18%). However, the tubes have often been found to become brittle and to rupture after having been in use for some time. A similar failing has been observed in the "pigtails" which are used to connect the outlets of the tubes to a header for the gas produced as a result of the steam reforming process. When a tube fails it is isolated from the rest of the tubes by squeezing, and thereby sealing, the pigtails connecting it to the inlet and outlet headers. However, if the outlet pigtail has become brittle it fractures when an attempt is made to squeeze it, and hence the reaction tube cannot conveniently be isolated, which means that the whole steam reforming unit has to be shut down whilst the tube which has failed is being replaced.

We believe that we have discovered at least one cause of this serious defect in steam reforming tubes and their outlet pigtails; and we have devised a method of preventing or at least reducing the risk of the defect occurring. We believe that in the presence of carbon containing substances (the hydrocarbon feedstock and/or the carbon oxides produced) at high temperatures carburisation of a tube or pigtail occurs, an inner layer of metal carbide being formed which not only renders the whole tube or pigtail brittle and may cause it to crack, but also makes it more susceptible to subsequent oxidation in the presence of the steam. Probably the trouble in reaction tubes is enhanced by any local overheating which may occur as a result, for example, of impingement of flames on the tubes.

Our invention is applicable not only to steam reforming tubes and pigtails but also to other furnaces and furnace tubes which are exposed to a carburising or carburising/oxidising environment, such as the tubes in ethylene furnaces.

According to our invention we provide a furnace or furnace tube made of an alloy of iron, nickel and/or cobalt containing at least 15% by weight of chromium and adapted for use in a carburising environment in chemical plant, characterised in that a surface to be exposed to the carburising environment is coated with a substantially inert material which forms a barrier to prevent or hinder carburisation of the alloy.

Carburisation becomes a more severe problem as the temperature is raised, and usually the problem is important only when the temperature is high, e.g. 600—1000° C. And at such temperatures it is necessary to use equipment which is made of special alloys which are designed to be capable of operating at high temperatures under conditions of stress and which are resistant to corrosion by oxidation. Thus our invention applies to an alloy of iron, nickel and/or cobalt, containing at least 15%, and preferably at least 18%, by weight of chromium.

The alloy may conveniently be a steel comprising iron, nickel and chromium and may also contain one or more other suitable ingredients such as for example manganese, tungsten, molybdenum, niobium, carbon or silicon.

Particularly suitable alloys include steels of the 25/20 and 18/37 chromium/nickel types.

The invention is particularly applicable to equipment such as ethylene furnaces or reaction tubes, and their pigtails, which are used in the process of steam reforming hydrocarbons to produce, for example, ammonia synthesis gas, methanol synthesis gas, town gas, hydrogen or carbonylation gas. Such equipment may have to operate at up to about 1000° C, and at this temperature the carburisation reaction is liable to proceed very readily unless the equipment is protected by means of our invention.

The coating must be of a substantially inert material, because it must not be chemically attacked by the materials with which it is in contact to form a substantial amount of any undesirable product, and must be capable of withstanding a high temperature.

The coating may itself be resistant to carburisation. For example the coating may comprise a non-metallic substance, such as for instance a vitreous enamel which is stable at high temperature, for example the product sold under the Registered Trade Mark "NUCERITE". Alternatively the coating may itself carburise but still act as a barrier to prevent or hinder carburisation of the underlying metal. Preferably the coating is a metallic material, and in particular aluminium, chromium or nickel.

The preferred thickness of the coating depends on the coating material used and the environment to which it is to be submitted; but generally a coating with a minimum thickness of 0.005 inch is found to be suitable.

The coating may be applied to the furnaces or furnace tubes by any convenient method, for example by spraying, painting, electrodeposition, deposition from the gas phase, high temperature transfer from the solid phase, or any type of lining or cladding method. In the case of aluminium or chromium which are the preferred materials to use, the coating is preferably applied by the known processes of aluminisation or chromisation. The latter techniques comprise contacting the surface to be treated with a mixture of powdered aluminium or chromium, an inert refractory material and a substance capable of forming a volatile compound with the aluminium or chromium, and heating the mixture and the surface with which it is in contact. The inert refractory material, which serves the purpose of separating the particles of the metallic powder and preventing them from coalescing, must not sinter on heating: it may conveniently comprise powdered alumina or chromia. The third ingredient of the mixture may conveniently be ammonium chloride, in which case aluminium or chromium chloride is formed and decomposes to form a metallic deposit on the metal surface. It is possible that the metallic deposit may not be aluminium or chromium but may be an alloy of one of these metals with the metal treated. An example of a particularly suitable mixture for aluminising steel is one comprising 15% of aluminium powder, 83% of alumina and 2% of ammonium chloride, the percentages being by weight. Satisfactory aluminisation can be achieved by heating such a mixture for about 20 hours at about 950° C.

The production of aluminised chromium steel suitable for use in a carburising environment in chemical plant is illustrated in the following examples.

EXAMPLES

The materials coated were high carbon varieties of 25/20 and 18/37 chromium/nickel type steels. Their analyses were as follows:—

	C	Cr	Ni	Mn	Si	Cu
25/20 alloy	0.38%	27.1%	20.0%	0.8%	1.35%	0.1%
18/37 alloy	0.43%	17.7%	38.2%	0.88%	0.79%	0.5%

The aluminising mixture consisted of aluminium powder, alumina and ammonium chloride, and three different proportions of aluminium and alumina were used.

The aluminisation process was carried out by heating in mild steel pots of 2 in. diameter and 3½ in. long having loose fitting lids each of which had an ⅛ in. vent hole. The pots were given a dummy run by heating with the aluminising mixture at 950° C to ensure that subsequently little aluminium was drawn from the mixture by the pots.

Steel specimens of approximately 1.7 in.^{2} surface area were ground and then degreased by acetone. Two specimens were treated in each pot. The pots were half filled with the aluminising powder which was then consolidated. The specimens were pressed half way in and the remainder of the powder added and consolidated, about ½ in. clearance being allowed from the lid. The lid was sealed with a paste of burnt clay.

The pots were placed in a furnace and heated at a fixed temperature for a measured

period of time. Details of the temperatures, times, and compositions of the aluminising mixture used are given in tables 1 and 2 below in respect of the two types of steel used. The tables also give the thicknesses of the coatings, which were determined by metallographical examination.

TABLE 1

25/20 Alloy

Aluminising Mixture			Temp.	Time	Coating thickness	Remarks
Al wt. %	Al_2O_3 wt. %	NH_4Cl wt. %	°C.	hrs.	in.	
25	73	2	850	20	*0.002	Thin brittle surface layer
			900	10	*0.005	Good but for thin rough surface layer
			900	20	*0.003	Fairly good
			950	20	*0.007	Good
			950	42	*0.006	Good
			1000	20	*0.0075	Good thick coating
15	83	2	900	10	0.002	Too thin
			900	20	0.003	Good clean coating
			950	10	0.003	Fairly good
			950	20	0.005	Good coating; reasonably thick
			1000	20	0.012	Good underneath; rough outer layer
			1000	20	0.007	Good but some surface roughness
5	93	2	1000	10	0.0035	Good but thin
			1000	20	0.004	Surface roughness
			1000	30	0.001	Very thin
			1050	20	0.003	Oxide penetration into metal occurred

TABLE 2

18/37 alloy

Aluminising Mixture			Temp.	Time	Coating thickness	Remarks
Al wt. %	Al_2O_3 wt. %	NH_4Cl wt. %	°C.	hrs.	in.	
25	73	2	850	20	*0.002	Too thin
			900	10	*0.006	
			900	20	*0.004	
			950	20	*0.005	Good coating
			950	42	*0.005	
			1000	20	*0.004	
					*0.008	
15	83	2	900	10	0.002	Too thin
			900	20	0.003	Good coating
			950	10	0.003	Good
			950	20	0.005	Good
			1000	20	0.007	Fairly good; small amount
			1000	20	0.005	of surface roughness
5	93	2	1000	10	0.0025	Too thin
			1000	20	0.0025	
			1000	30	0.001	Coatings appeared to have
			1050	20	0.0035	oxidised

* All these samples had to some degree a rough friable outer layer, the thickness of which is not included.

It was concluded that in general the aluminising mixture containing 25% of aluminium gave fairly thick coatings but brittle outer surface layers were formed, the best results being obtained at 900—950° C. With the mixture containing 15% of aluminium good coatings were obtained at 900—950° C, the preferred time being 20 hours. Some surface roughness occurred at 1000° C with this mixture. The mixture containing 5% aluminium gave very clean coatings but these were thin and appeared weak. At 1050° C oxide penetration along grain boundaries of the base metal occurred.

The hardness of the coatings was measured and hardness figures of up to 950 Vickers hardness were obtained just inside the surface of the coatings, whereas near the base metal the figures fell to about 500 Vickers hardness.

To give an indication of the likely service behaviour of the various coatings the coated samples were heated in air for 90 hours at 1000° C. The coatings up to 0.003 in. thick appeared to break down during the tests because the surfaces of the specimens had a rough black oxidised appearance. Above a thickness of 0.003 in. the coatings appeared to withstand the heat treatment satisfactorily. Those samples which had a coarse outer coating lost it by spalling during the tests and they appeared very clean. Microexamination after the heating treatment suggested that some diffusion of the aluminium into the base metal had occurred, and the hardness of the coatings were less, when the 25/20 alloy was used. The coatings on the 18/37 alloy appeared to be very little affected by the heat treatment.

From the above experiments it was concluded that the best results were obtained when the 18/37 alloy was heated with a 15/83/2 aluminising mixture for 20 hours at 950° C.

It was noticed in the experiments that the coating thickness appeared to be little affected by the ratio of the volume of the aluminising powder to the surface area of the metal treated. The composition of the mixture was a much more important factor.

A 12 in. length of 1 in. diameter tube made of the 18/37 alloy was packed with the 15/83/2 aluminising mixture and the ends of the tube sealed with metal plugs and a burnt clay paste, each end having an $\frac{1}{8}$ in. vent hole. This assembly was heated to 950° C for 20 hours. The coating produced was satisfactory, being about 0.007 in. thick, and had a hardness of 950/1000 Vickers hardness.

WHAT WE CLAIM IS:—

1. A furnace or furnace tube made of an alloy of iron, nickel and/or cobalt containing at least 15% by weight of chromium and adapted for use in a carburising environment in chemical plant, characterised in that a surface to be exposed to the carburising environment is coated with a substantially inert material which forms a barrier to prevent or hinder carburisation of the alloy.

2. A furnace or furnace tube according to Claim 1 in which the chromium content is at least 18% by weight.

3. A furnace or furnace tube according to Claim 2 which is made of steel of the 25/50 or 18/37 chromium/nickel type.

4. A furnace or furnace tube according to any one of the preceding claims in which the coating comprises a vitreous enamel which is stable at high temperature.

5. A furnace or furnace tube according to any one of Claims 1 to 3 in which the coating comprises aluminium, chromium or nickel.

6. A furnace or furnace tube according to any one of the preceding claims in which the thickness of the coating is at least 0.005 inch.

7. A furnace or furnace tube according to any one of the preceding claims which comprises a reaction tube and/or its inlet and/or outlet pigtail, which is intended for use in the process of steam reforming hydrocarbons.

8. An ethylene furnace according to any one of Claims 1 to 6.

9. A method of protecting against carburisation a furnace or furnace tube made of an alloy of iron, nickel and/or cobalt containing at least 15% by weight of chromium and adapted for use in a carburising environment in chemical plant, comprising applying a protective coating by the process of aluminisation or chromisation.

10. Methods according to Claim 9 for protecting against carburisation a furnace or furnace tube substantially as described herein and with reference to the Examples.

11. A furnace or furnace tube intended for use in a carburising environment in chemical plant when protected against carburisation by a method according to either Claim 9 or Claim 10.

12. A process of steam reforming hydrocarbons which is carried out using reforming tubes and/or inlet and/or outlet pigtails according to Claim 7.

13. A process for producing ethylene from hydrocarbons which is carried out using an ethylene furnace according to Claim 8.

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